Mathematical modelling of stress distributions in batteries

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Mathematical Institute

Oxford Mathematics

Battery modelling

Mathematicians

Oxford - Jon Chapman, Alain Goriely, John Ockendon, Peter Howell, Jeevan Chakraborty, Cameron Hall, Chang Wang

Southampton –Giles Richardson, Jamie Foster, Rahifa Ranom

QUT Brisbane – Troy Farrell, Stephen Dargaville

Chemists

Southampton – John Owen

Nexeon Ltd Bill Macklin, Mike Lain

Alkaline batteries

Li-ion batteries

Battery modelling

Some design considerations:

SAFETY!!!!!!!

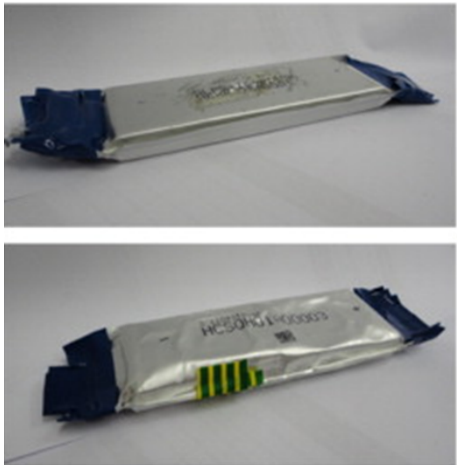
Rapid charging

Energy storage per kilogram

Maximum power of discharge

Long life recharging/discharging

SAFETY!!!!!!!



Yufit et al., Electrochemistry Communications,13, 2011, pp608-610

Alkaline batteries

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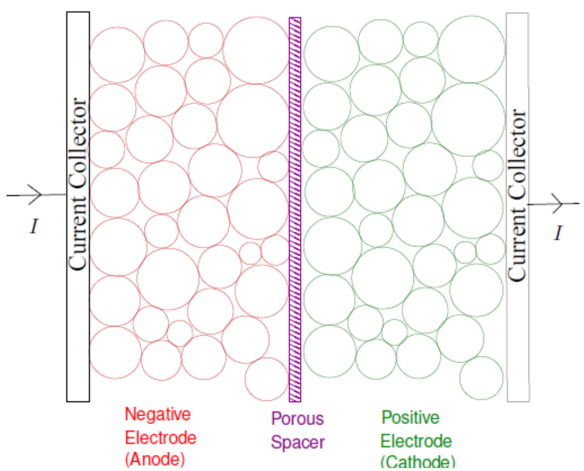
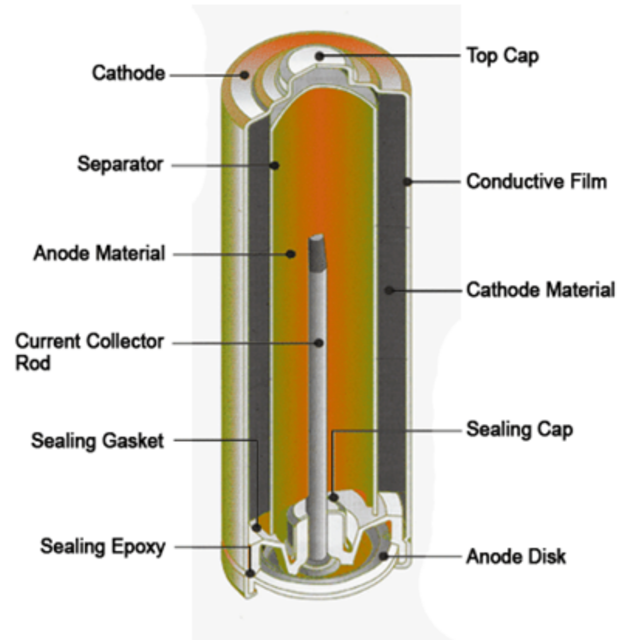
- Active ingredient is in the cathode – magnesium oxide
- Cathode is usually carbon
- “non-rechargable”





Basic structure of alkaline battery

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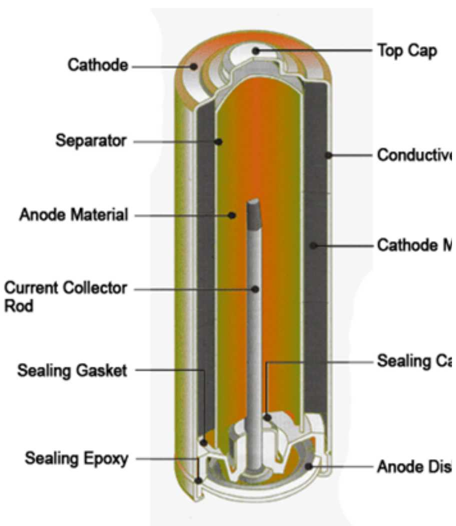
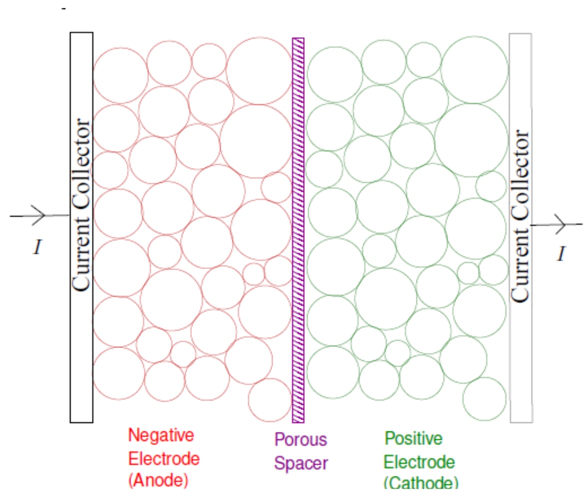
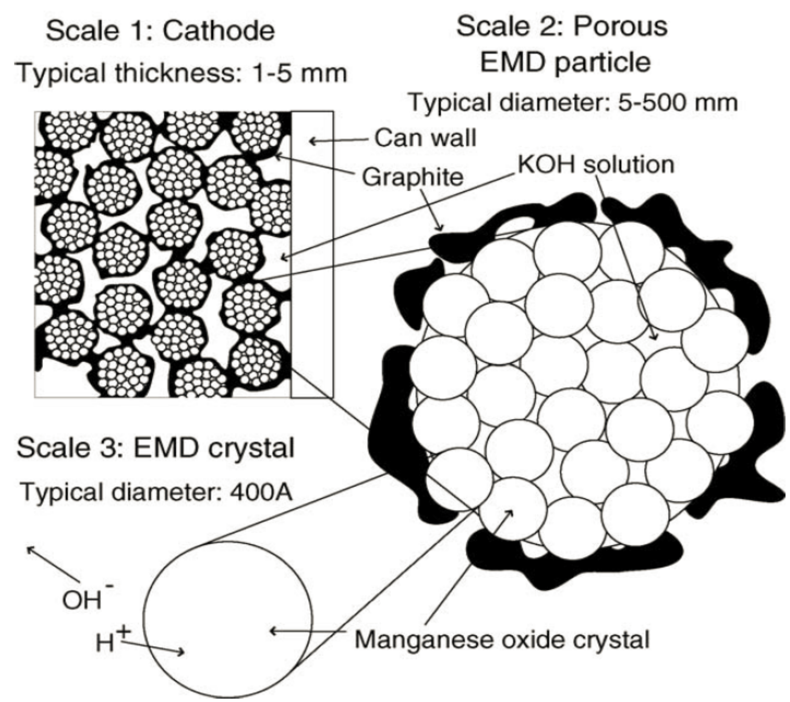




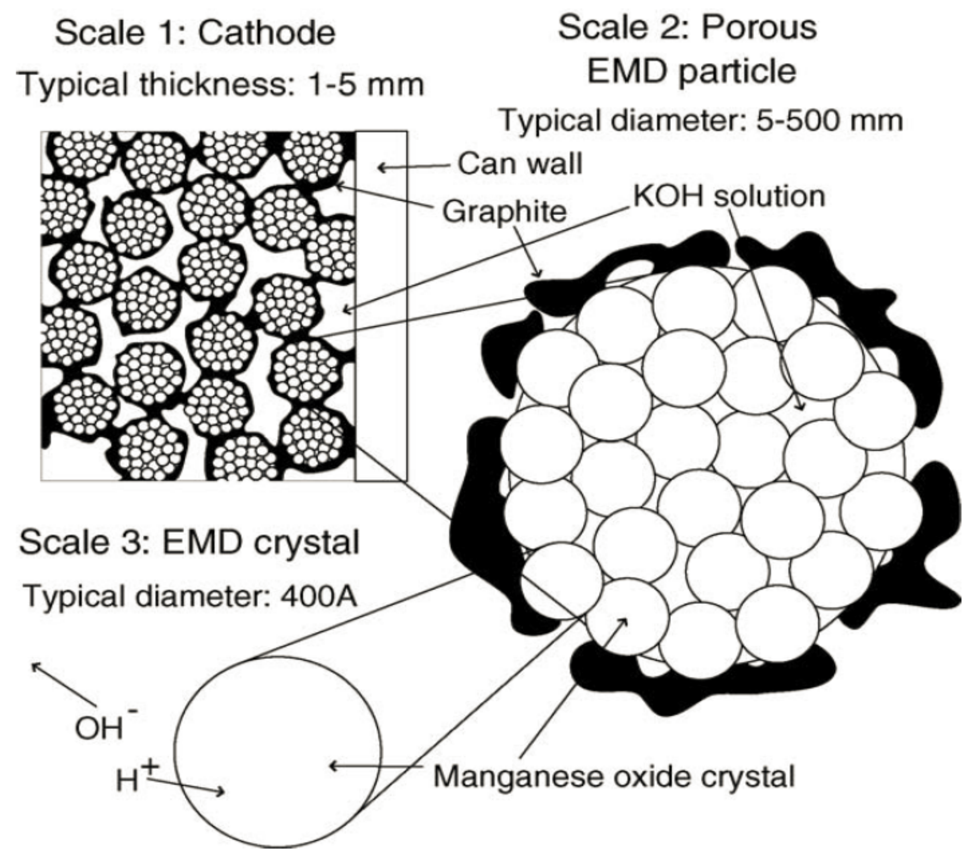
Idealised geometry



Different scales

Modelling of behaviour of Alkaline batteries

- Electron flow through the solid matrix: ohmic
- Transport of species in the solid: diffusion
- Reaction at the solid/electrolyte interface: Butler Volmer
- Transport through the electrolyte: concentrated theory
- Separator and anode behaviour



General issues in modelling batteries

- Carbon to create electrically connected matrix but remain small volume
- Large salt concentrations to make easy electrolyte transport and avoid depletion but also avoid precipitation
- Small crystals to reduce distance for species to diffuse

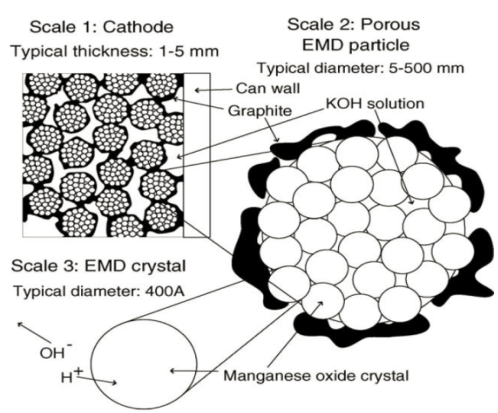
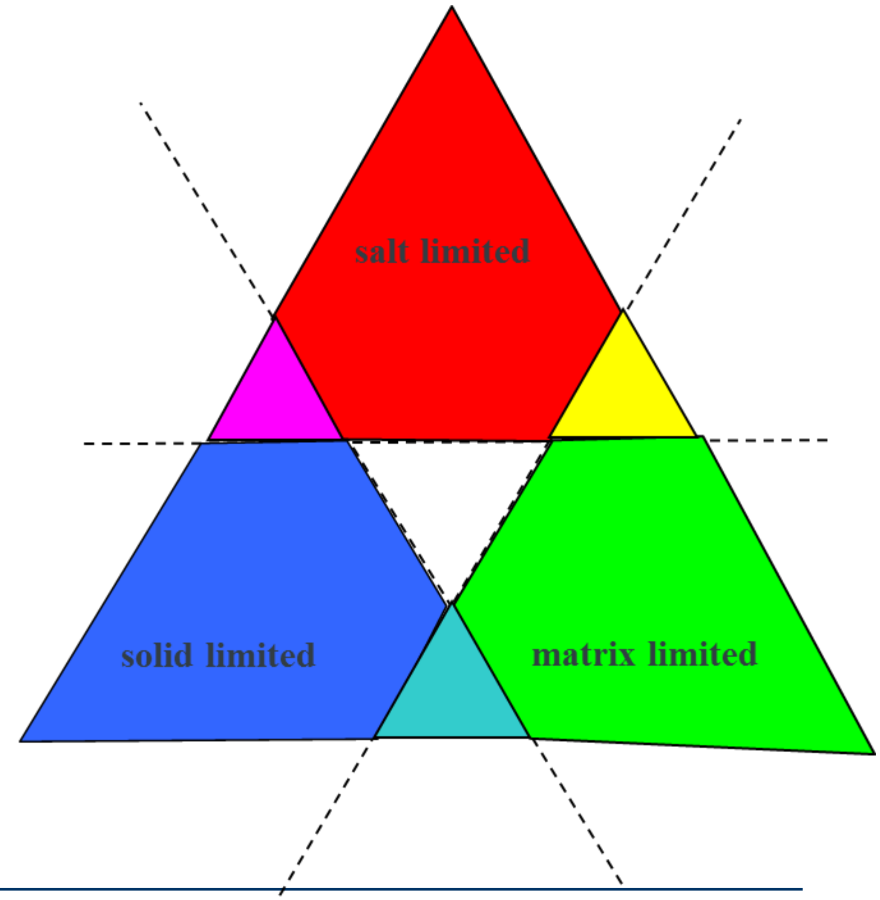


Diagram courtesy of John Owen



General issues in modelling of Alkaline batteries

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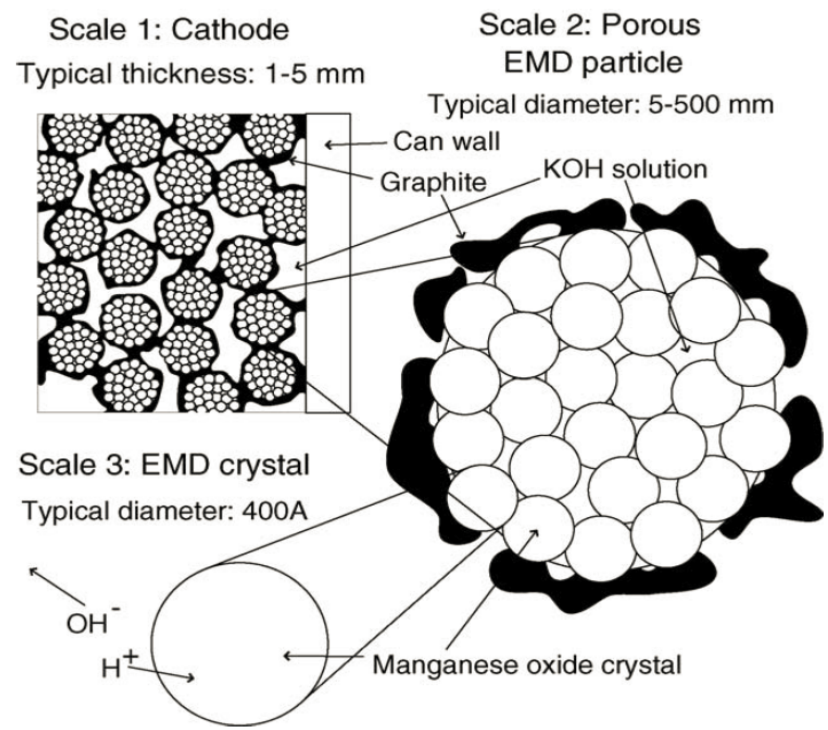
- Large numbers of particles – homogenisation to create "Newman" models (averaged over particles)
- Many extensions: such as three different scales



General issues in modelling of Alkaline batteries

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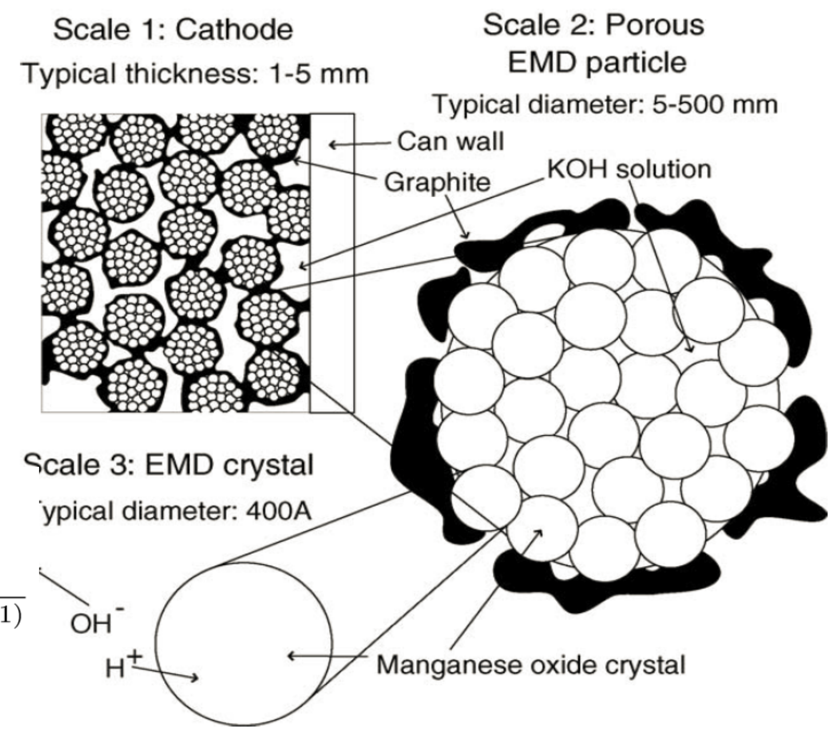
Bulter-Volmer – OCV (solid concentrations / electrolyte concentrations

$$i_0 \left(\exp\left(\frac{\alpha_{\mathrm{a}} F}{R\ T}(\phi_s - \phi_e - U) \right) - \exp\left(\frac{-\alpha_{\mathrm{c}} F}{R\ T}(\phi_s - \phi_e - U) \right) \right)$$



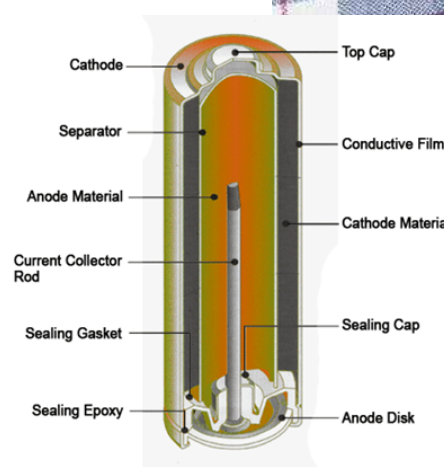
$$\begin{aligned} U(c_{\mathrm{s}}, c_{\mathrm{e}}) = {} & \frac{RT}{F(\alpha_{\mathrm{a}} + \alpha_{\mathrm{c}})} \ln \left(\frac{c_{\mathrm{e}}(c_{\mathrm{s,max}} - c_{\mathrm{s}})}{c_{\mathrm{s}}} \right) + a_0 \\ & + a_1 \frac{1}{1 + \mathrm{e}^{\alpha_1 \left(\frac{c_{\mathrm{s}}}{c_{\mathrm{s,max}}} - \beta_1 \right)}} + a_2 \frac{1}{1 + \mathrm{e}^{\alpha_2 \left(\frac{c_{\mathrm{s}}}{c_{\mathrm{s,max}}} - \beta_2 \right)}} + a_3 \frac{1}{1 + \mathrm{e}^{\alpha_3 \left(\frac{c_{\mathrm{s}}}{c_{\mathrm{s,max}}} - 1 \right)}} \\ & + a_4 \frac{1}{1 + \mathrm{e}^{\alpha_4 \frac{c_{\mathrm{s}}}{c_{\mathrm{s,max}}}}} + a_5 \frac{c_{\mathrm{s}}}{c_{\mathrm{s,max}}} + \sum_{i=1}^{M} b_i c_{\mathrm{e}}^i, \end{aligned}$$

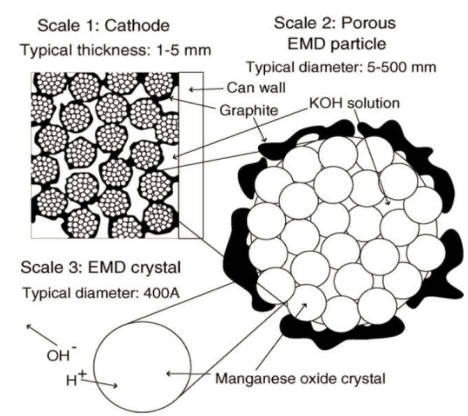
$$i_0(c_{\mathrm{s}}, c_{\mathrm{e}}) = k c_{\mathrm{e}}^{\frac{\alpha_{\mathrm{a}}}{\alpha_{\mathrm{a}} + \alpha_{\mathrm{c}}}} \ (c_{\mathrm{s,max}} - c_{\mathrm{s}})^{\frac{\alpha_{\mathrm{a}}}{\alpha_{\mathrm{a}} + \alpha_{\mathrm{c}}}} \ c_{\mathrm{s}}^{\frac{\alpha_{\mathrm{c}}}{\alpha_{\mathrm{a}} + \alpha_{\mathrm{c}}}}$$

Uses ides of Nernst plus lattice site energies/interaction energies (Howey et al)
Lack of transfer current data: allow for depletion

Modelling of behaviour of Alkaline batteries

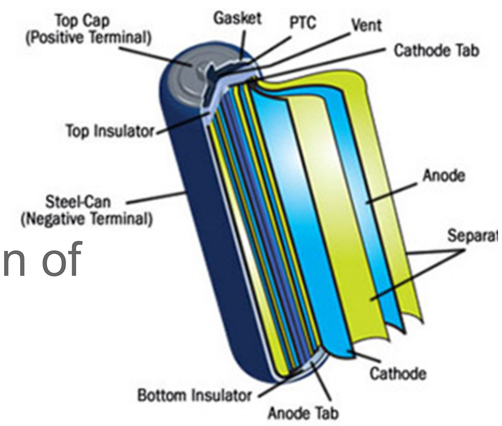
- Damage from leaking alkaline batteries
- Possible poor manufacture/sealing
- Manganese dioxide expands by ~10% on discharge
- Stresses induced by confinement
- Changes in particle or cathode porosity

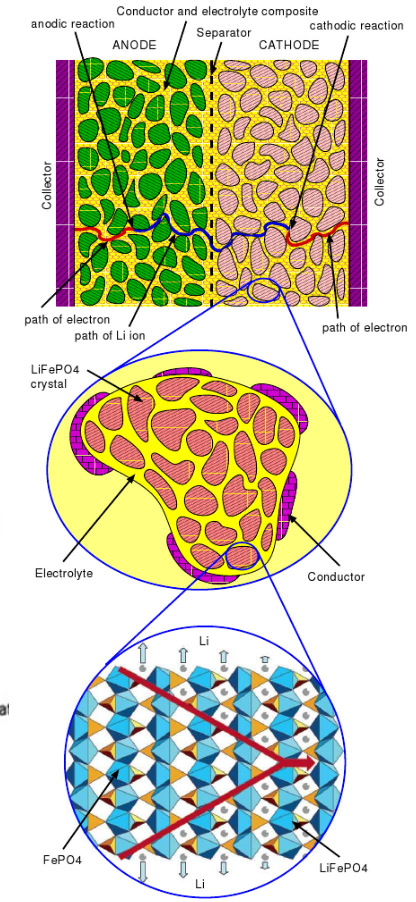




Lithium-ion batteries

- Structures has three scales - cathode/particle/crystal (crystal=particle?)
- Very small distances between current collectors
  - Electron conduction through matrix
  - Transport of intercalated Lithium in solid
  - Intercalation reaction at solid/electrolyte interface
  - Transport in electrolyte
- OCV of many cathode materials is very flat – makes tracking State of Charge (SOC) very difficult
- Models needed to infer SOC and deterioration of battery





Lithium-ion batteries

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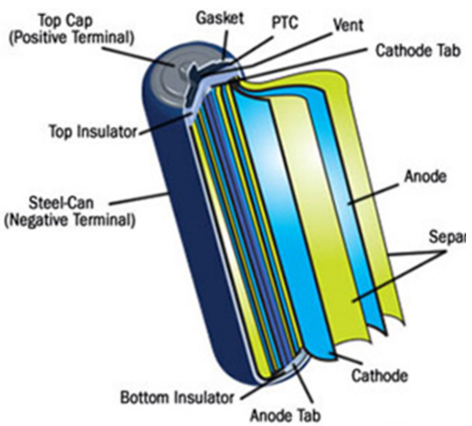
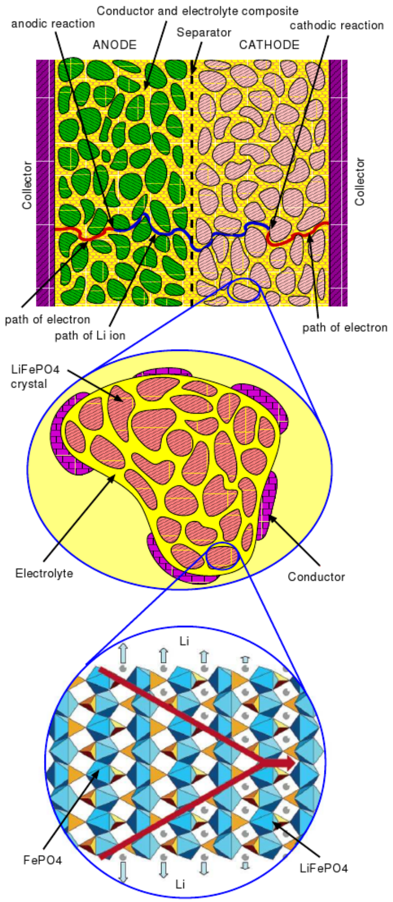
- Cathode material swells with Lithium
- Transport of intercalated lithium is significantly affected by mechanical stresses
- Reaction at surface is dependent on mechanical stresses
- SEI (Solid electrolyte interface) gets deformed and may fracture/buckle





Silicon as a anode material: Nexeon

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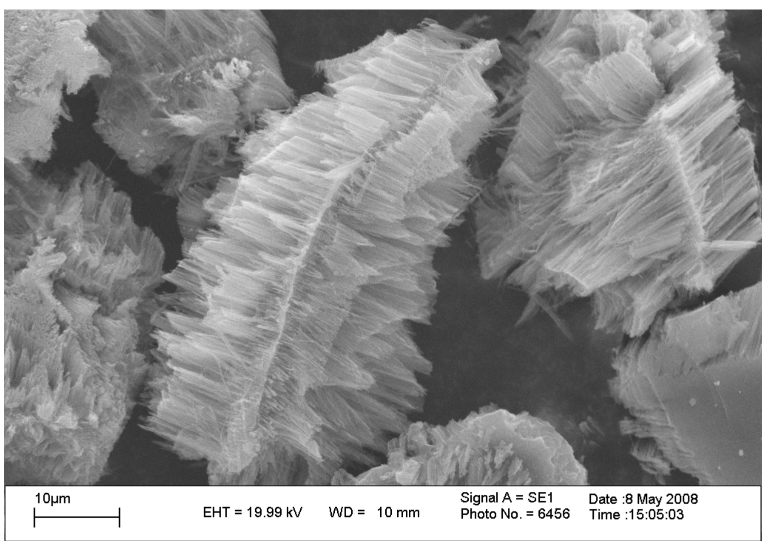
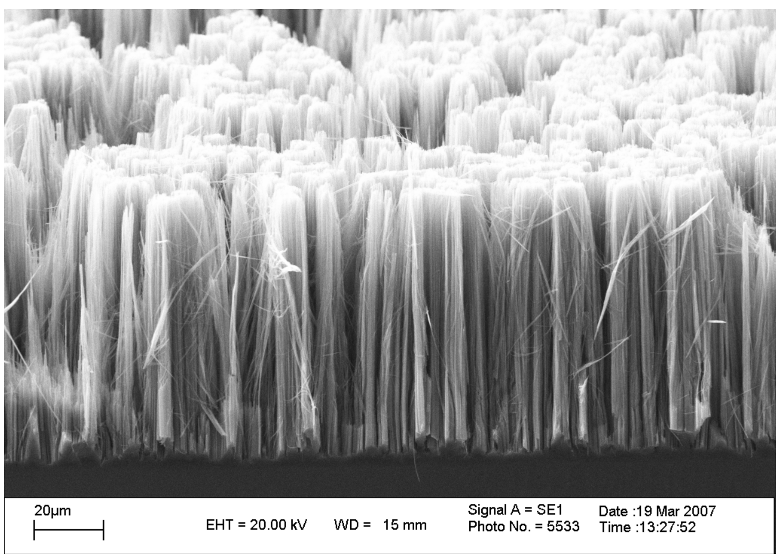
- Silicon – stores 6 time the energy per kilogram compared to carbon
- Silicon swells up to 3 times its volume by intercalation
- Mechanical stresses due to swelling – causes fracture of particles and loss of electrical connection





Nano structure to avoid large concentration (volume increase) gradients in the solid

Silicon as a anode material: Nexeon

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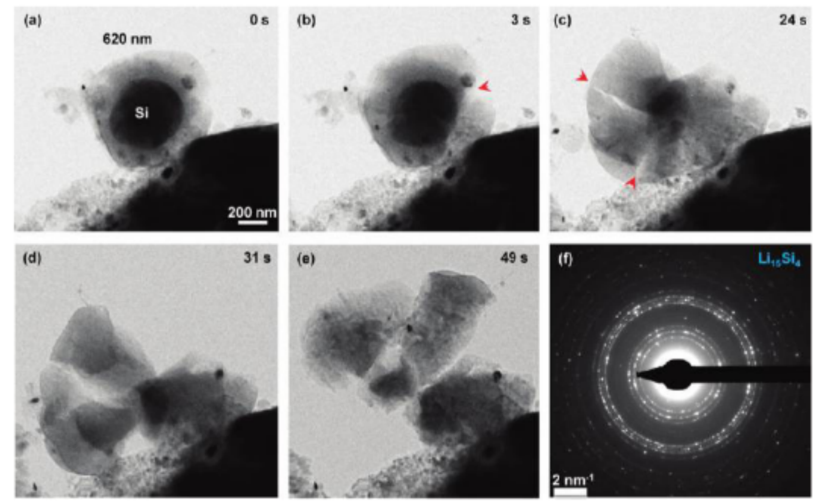
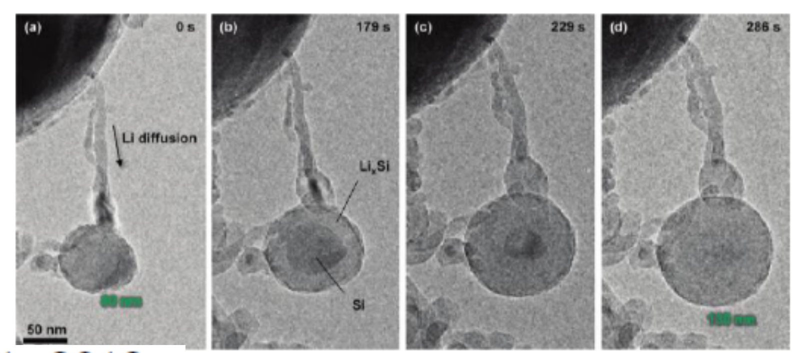
Nano structures prevent large concentration (volume increase) gradients in the solid





Reproduced from Liu *et al.*, ACS Nano, 6, 1522–1531, 2012.

Strategies for avoiding mechanical stresses

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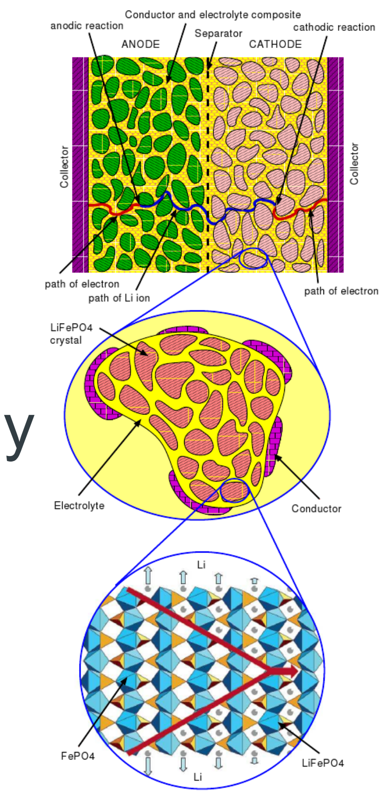
- Only create small concentration gradients in the solid
  - Nanostructures
  - Very high matrix conductivity
  - Very small distances between current collectors
- Constrain the solid so that it swells in a controlled way
  - Use the crystal parts of the solid as these are highly anisotropic
    - when lithium intercalates at high concentrations the solid becomes amorphous and isotropic
  - Use other harder materials



Stresses within anode materials

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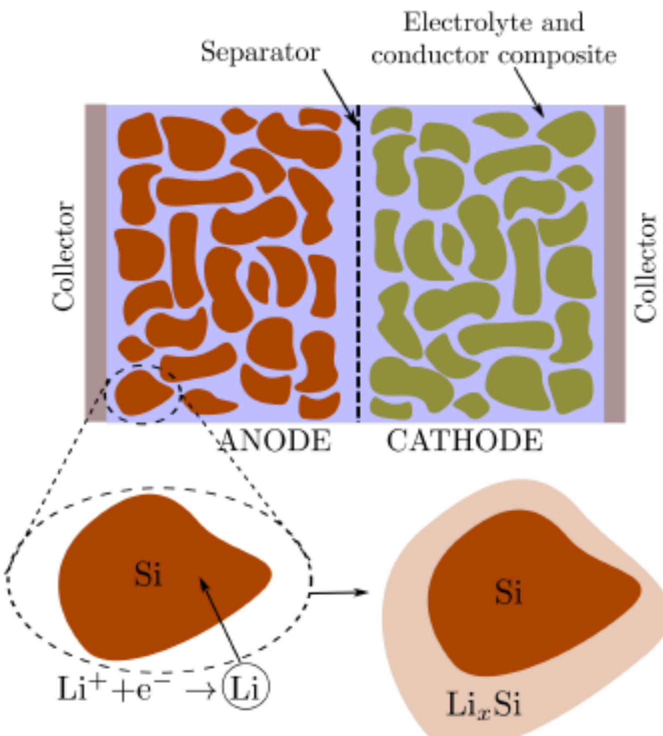
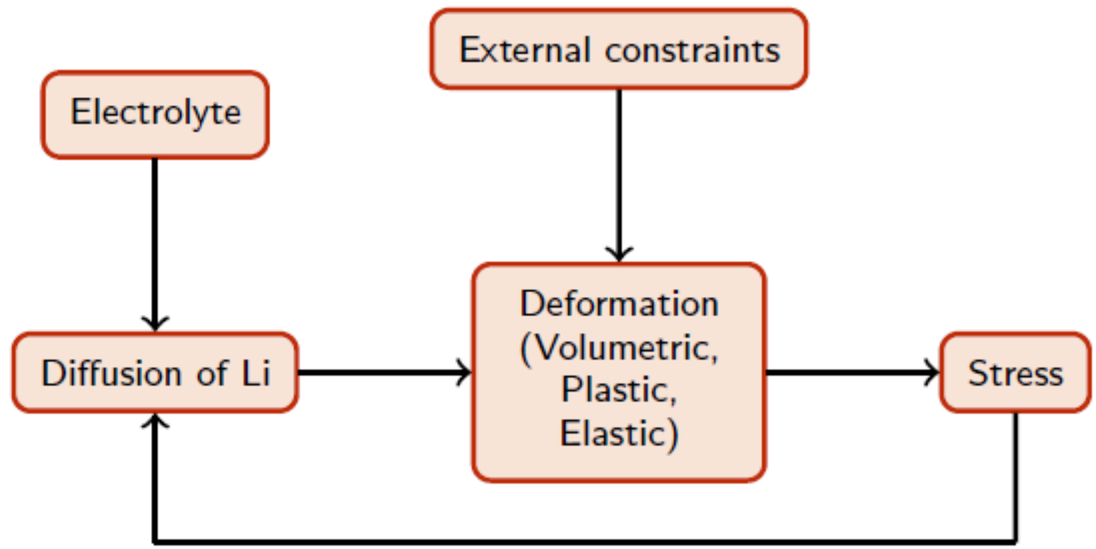


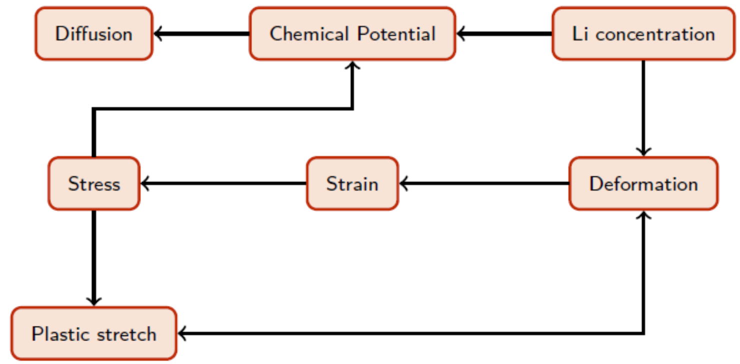


Total deformation due to 3 effects: Volume increase, elastic deformation, plastic deformation

Modelling deformation of crystals

Model of Chakraborty et al

- Large deformations
- Chemical potential depends on concentration and stress
- Deformations are described as product of three deformation gradient tensors
- Strain energy and plasticity laws



$$\boldsymbol{j} = -Dc\boldsymbol{\nabla}\mu$$
$$\mu = \mu_{\text{conc}} + \mu_{\text{stress}}$$
$$\mu_{\text{conc}} = \mu^0_{\text{conc}} + \log(\gamma c)$$
$$\mu_{\text{stress}} = \frac{\partial W}{\partial c}$$

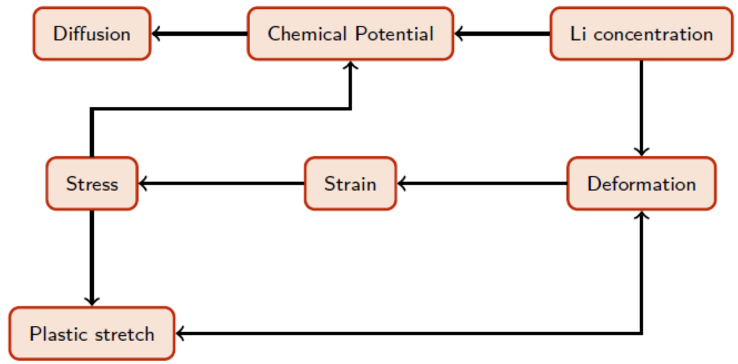
$$\boldsymbol{\sigma}^0 = \frac{\partial W}{\partial \mathbf{F}} = f(c, \mathbf{E}^e)$$
$$\mathbf{F} = \mathbf{F}^c\mathbf{F}^p\mathbf{F}^e = \mathbf{I} + \boldsymbol{\nabla}\boldsymbol{u}$$
$$\mathbf{E}^e = \frac{1}{2}\left(\mathbf{F}^{eT}\mathbf{F}^e - \mathbf{I}\right)$$
$$\mathbf{F}^c = (1 + 3\bar{\eta}c)^{1/3}\mathbf{I}$$

$$\mathbf{F}^p = g(\boldsymbol{\sigma}^{\mathbf{0}})?$$
$$\det(\mathbf{F}^p) = 1$$

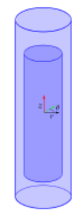
Modelling deformation of crystals

Model of Chakraborty et al

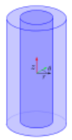
- Applied to single rod of amorphous material
- Constrained and unconstrained cases
- Main issues
  - where is plastic yield stress reached during charging – rate dependent
  - possible buckling when constrained



$$\boldsymbol{j} = -Dc\boldsymbol{\nabla}\mu$$
$$\mu = \mu_{\text{conc}} + \mu_{\text{stress}}$$
$$\mu_{\text{conc}} = \mu^0_{\text{conc}} + \log(\gamma c)$$
$$\mu_{\text{stress}} = \frac{\partial W}{\partial c}$$



Net axial force is zero.



Net axial displacement is zero.

$$\boldsymbol{\sigma}^0 = \frac{\partial W}{\partial \mathbf{F}} = f(c, \mathbf{E}^e)$$
$$\mathbf{F} = \mathbf{F}^c\mathbf{F}^p\mathbf{F}^e = \mathbf{I} + \boldsymbol{\nabla}\boldsymbol{u}$$
$$\mathbf{E}^e = \frac{1}{2}\left(\mathbf{F}^{eT}\mathbf{F}^e - \mathbf{I}\right)$$
$$\mathbf{F}^c = (1 + 3\bar{\eta}c)^{1/3}\mathbf{I}$$

$$\mathbf{F}^p = g(\boldsymbol{\sigma}^0)?$$
$$\det(\mathbf{F}^p) = 1$$

Modelling constrained rod

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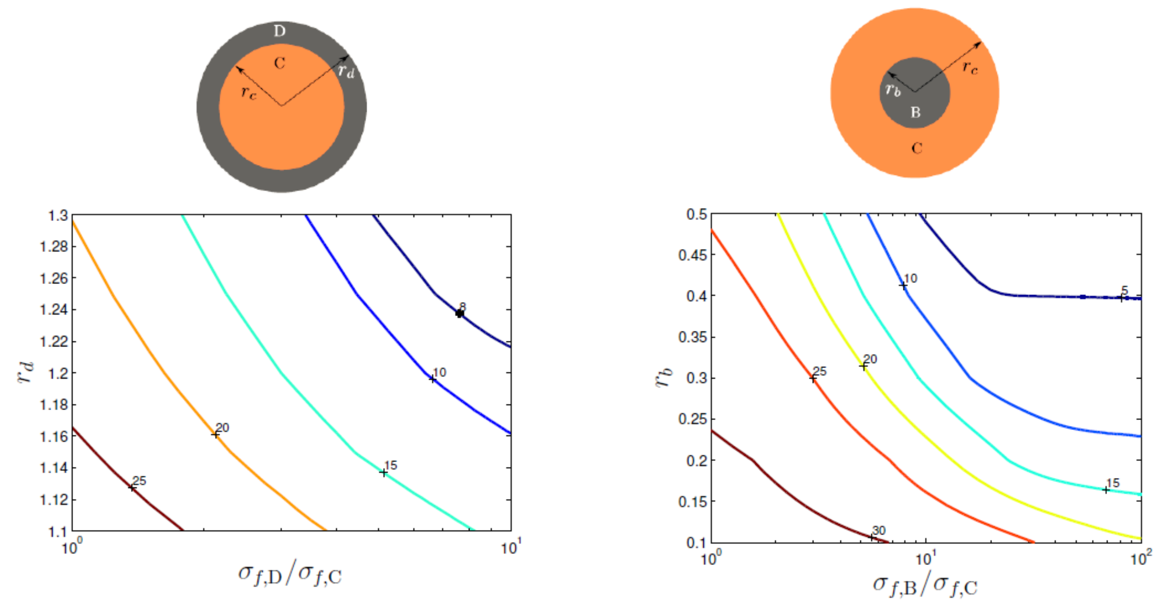
- Idealised rod no external forces
- Silicon with a similar stronger material acting as a constraint
- Constraint has higher yield stress, same elasticity, and no volume increase



Outer constraint **Inner constraint**

Yield stress of Region D: $\sigma_{f,\mathrm{D}}$ Yield stress of Region C: $\sigma_{f,\mathrm{C}}$ Yield stress of Region B: $\sigma_{f,\mathrm{B}}$

Contour values indicate percentage increase in length

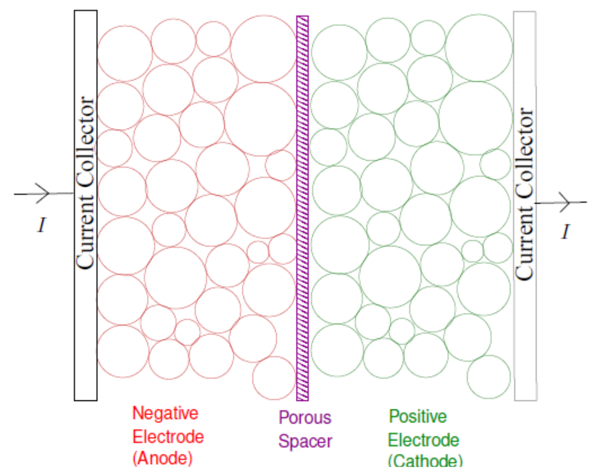
Homogenisation theory

Extending ideas to the macroscale

Assume

- Dilute electrolyte
- Perfectly conducting matrix
- Uniform size particles with no smaller scale crystals
- Small deformations (linear theory)

Ω_{a}	:	Anode
Ω_{el}	:	Electrolyte
$\partial\Omega_{\mathrm{ael}}$	:	Boundary between anode and electrolyte
c_{a}	:	Concentration of lithium in anode particles
c_{el}	:	Concentration of lithium ions in electrolyte
ϕ	:	Electric potential
$\bar{\boldsymbol{\sigma}} = \bar{\eta}\boldsymbol{\sigma}$	:	Stress
$\bar{\boldsymbol{u}} = \bar{\eta}\boldsymbol{u}$	:	Displacement



Homogenisation theory

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In particles:

- Linear elasticity
- Concentration and stress induced diffusion

$$\left.\begin{aligned}
\boldsymbol{\nabla}\cdot\bar{\boldsymbol{\sigma}} &= 0,\\
\bar{\boldsymbol{\sigma}} &= \mathbb{C}:\bar{\mathbf{E}}^{e} = \mathbb{C}:(\boldsymbol{\nabla}\bar{\boldsymbol{u}} - c_{\mathrm{a}}\mathbf{1}),\\
\frac{\partial c_{\mathrm{a}}}{\partial t} &= -\epsilon\boldsymbol{\nabla}\cdot\boldsymbol{j}_{\mathrm{a}},\\
\boldsymbol{j}_{\mathrm{a}} &= -\frac{\gamma\vartheta}{\epsilon}\kappa_{\mathrm{a}}\left[\boldsymbol{\nabla}c_{\mathrm{a}} - \mathrm{S_d}c_{\mathrm{a}}\boldsymbol{\nabla}\{\mathrm{tr}(\bar{\sigma})\}\right],
\end{aligned}\right\}\quad \text{in } \Omega_{\mathrm{a}}$$

In electrolyte:

- Dilute theory

$$\left.\begin{aligned}
\frac{\partial c_{\mathrm{el}}}{\partial t} &= -\boldsymbol{\nabla}\cdot\boldsymbol{j}_{\mathrm{el}},\\
\boldsymbol{j}_{\mathrm{el}} &= -D\boldsymbol{\nabla}c_{\mathrm{el}},\\
0 &= \boldsymbol{\nabla}\cdot\boldsymbol{j}_{\mathrm{f}},\\
\boldsymbol{j}_{\mathrm{f}} &= -D\left(\zeta c_{\mathrm{el}}\boldsymbol{\nabla}\phi - \alpha\boldsymbol{\nabla}c_{\mathrm{el}}\right),
\end{aligned}\right\}\quad \text{in } \Omega_{\mathrm{el}}$$

At interfaces:

- Usual continuities
- Simple Butler Volmer with stresses

$$\left.\begin{aligned}
\bar{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{n}} &= 0,\\
\boldsymbol{j}_{\mathrm{a}}\cdot\hat{\boldsymbol{n}} &= Q_{\mathrm{a}},\\
\boldsymbol{j}_{\mathrm{el}}\cdot\hat{\boldsymbol{n}} &= \epsilon k Q_{\mathrm{a}},\\
\boldsymbol{j}_{\mathrm{f}}\cdot\hat{\boldsymbol{n}} &= \epsilon k(1-\alpha)Q_{\mathrm{a}},\\
Q_{\mathrm{a}} &= \mathrm{M}c_{\mathrm{el}}^{\frac{1}{2}}(1-c_{\mathrm{a}})^{\frac{1}{2}}c_{\mathrm{a}}^{\frac{1}{2}}\left[\exp\left\{-\frac{\zeta}{2}(\phi-U) - \frac{1}{2}\mathrm{S_d}\mathrm{tr}(\boldsymbol{\sigma})\right\}\right.\\
&\quad\left.-\exp\left\{\frac{\zeta}{2}(\phi-U) - \frac{1}{2}\mathrm{S_d}\mathrm{tr}(\boldsymbol{\sigma})\right\}\right],
\end{aligned}\right\}\quad \text{on } \partial\Omega_{\mathrm{ael}}$$

Homogenisation theory

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- Multiple scale (anode vs particle) give averaged equations. (Newman with stress)
- Simplest case is when particles are very small so concentration is uniform in particle
- Parameters in problem are derived from particle geometry and physical properties

$$\Phi \frac{\partial c_{\mathrm{el}}^{(0)}}{\partial t} = D\boldsymbol{\nabla} \cdot \left(\mathbf{B} \cdot \boldsymbol{\nabla} c_{\mathrm{el}}^{(0)}\right) + k\tilde{Q}_{\mathrm{a}},$$

$$D\boldsymbol{\nabla} \cdot \left\{\mathbf{B} \cdot \left(\zeta c_{\mathrm{el}}^{(0)} \boldsymbol{\nabla} \phi^{(0)} - \alpha \boldsymbol{\nabla} c_{\mathrm{el}}^{(0)}\right)\right\} = -k(1-\alpha)\tilde{Q}_{\mathrm{a}},$$

$$(1-\Phi)\frac{\partial c_{\mathrm{a}}^{(0)}}{\partial t} = -\tilde{Q}_{\mathrm{a}},$$

$$\boldsymbol{\nabla} \cdot \left(\mathbb{C}_{\mathrm{eff}} : \boldsymbol{\nabla} \bar{\boldsymbol{u}}^{(0)} - \mathbf{K} c_{\mathrm{a}}^{(0)}\right) = 0.$$

Summary

Getting good descriptions of OCV and transfer currents is needed to improve predictive models

Stresses induced within a battery can affect its performance

- micro-scale and macro-scale damage
- altering porosity
- Changing reaction rates at surfaces
- transporting species in solids